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A new type of polytopic coordination compound: The synthesis and NMR studies of the first hybrid thiacalix[4]arenoclathrochelates

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ABSTRACT

Nucleophilic substitution of the reactive chlorine atoms of iron(II) dichloroclathrochelate with thiol-terminated thiacalix[4]arene nucleophiles in the 1,3-*alternate* conformation afforded the first hybrid calixarenoclathrochelates with both ring-closed and ring-opened structures. The 1:1, 1:2 and 1:3 condensations of tetra-*O*-substituted thiacalix[4]arenes with thiol-terminated spacer substituents at the lower rim of the macrocyclic platform were performed. These thiol-terminated calixarene precursors were obtained from their *O*-ω-bromoalkyl precursors in the 1,3-*alternate* conformation, which are the products of alkylation of the parent thiacalix[4]arene with a series of homological α,ω-dibromoalkanes. The complexes obtained were characterized using elemental analysis, MALDI-TOF and ESI mass spectrometry, IR, ^{1}H, ^{19}F, ^{11}B and $^{13}C\{^{1}H\}$ NMR spectra; their molecular structures in solution were thoroughly studied by one- and two-dimensional NMR spectroscopy as well as by molecular mechanics calculations. The formation of the thiacalix[4]arenoclathrochelates depends on the length of their ribbed spacer substituents in the chelate α-dioximate fragments of the cage frameworks; those with four bridging methylene groups seem to be optimal for the synthesis of the ring-closed hybrid molecules with two metal-encapsulating macrobicycles.

1. Introduction

The design of novel nanosized polytopic molecular and supramolecular systems and devices and the study of their physicochemical properties are important areas of modern macrocyclic and supramolecular chemistry. Such compounds may be used to develop new materials for various applications, including molecular electronics and photonics, catalysis, modern pharmaceuticals, etc. [1]. Nanosized polytopic molecular systems usually contain several relatively independent building blocks that are connected either covalently or via hydrogen bonds, Coulombic and other weak intermolecular interactions. These building blocks perform a variety of complementary functions such as molecular recognition, signaling, photoconversion, accumulation and dissipation of energy. The most efficient synthetic pathway to these systems is based on the "bottom-up" principle using the appropriate molecular precursors.

One of the most promising types of these precursors that could be used to create multifunctional and polytopic molecular and supramolecular systems are calix[4]arenes (**1**, Scheme 1), which are macrocyclic molecules formed by phenolic units linked by bridging methylene groups [1c]. The thiacalix[4]arenes (**2**, Scheme 1) belong to the second generation of the calix[4]arene platforms [2]. Their most important advantages for the design of spatially preorganized systems with improved receptor and amphiphilic properties are: (i) the possibility to accommodate small hydrophobic organic molecules into the molecular cavities with the formation of stable host–guest assemblies; (ii) the variety of their conformations (*cone*, *partial cone*, 1,2- and 1,3-*alternate*, Scheme 1); (iii) unique possibilities to decorate both the upper and lower rims of these macrocyclic platforms by suitable donor and functionalizing groups to give molecular systems with several binding sites. Moreover, the bridging sulfur atoms of the thicalix[4]arenes may coordinate to metal ions, leading to complexes with a wide range of novel *O*,*S*-donor ligands [2]. Therefore, the thiacalixarene molecular scaffolds may be used to create numerous compounds–precursors of the more sophisticated nanosized molecular and supramolecular systems (in particular, hybrid and polytopic compounds) [3].

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